

UDC 666.5

EFFECT OF THE MOLDING METHOD ON THE STRUCTURE OF PORCELAIN ARTICLES

T. L. Neklyudova¹ and A. I. Zakharov²

Translated from *Steklo i Keramika*, No. 7, pp. 28–33, July, 2013.

The characteristic structural features of porcelain articles molded by different methods are studied. It is shown that the molding method can be identified. It is noted that the structure of the molded article affects the formation of a glaze layer. It is confirmed that the structure of the finished article inherits the texture of the initial paste.

Key words: porcelain, structure, molding methods.

Possessing relatively high strength, chemical stability, heat resistance and aesthetic properties of whiteness and translucence porcelain is widely used for household and technical articles. An important feature of the raw mixtures for porcelain production is a significant content of plastic clayey components, which makes it possible to mold articles by all of the main methods: slip casting, plastic molding and semidry pressing. The particles of the clayey and stony components of porcelain pastes have mostly non-isometric shapes, as a result of which they become oriented in accordance with the shear stresses of molding, forming pronounced textures.

The appearance of deformation and cracks in articles obtained by plastic molding — rolling, extrusion and stamping [1] — is often associated with the direction of texturing.

Texture is also observed to form with other methods of molding. For example, in slip casting the particles of clayey minerals near the surface of a gypsum mold were observed to be oriented [2]. Molding methods such as pressing, in which significant forces are applied to high-viscosity systems, lead to a more nonuniform stress field, where the stresses are fixed by the orientation of the particles of clayey and stony materials. The shape of an article plays a significant role; it determines the uniformity of the applied molding forces [3].

The stresses and densities inside an intermediate article become redistributed as a result of the clayey binder and this process requires time. Disperse anisotropic particles of clayey

minerals, surrounded by water shells and forming a plastic binder for grains of stony filler, in many ways make the system more mobile in different molding methods. At the same time the surface of the intermediate product at all stages (molding, drying and firing) is characterized to one degree or another by nonuniform open porosity and therefore nonuniformity. As the amount of binder increases, the viscosity of the system and the degree of surface nonuniformity of the intermediate article decrease [4].

The properties of ceramic materials are largely determined by their structure. The content and properties of the glass phase as well as the amount, size and shape of the crystalline formations — quartz, mullite and cristobalite — and their distribution have a considerable effect on the properties of porcelain articles. Even Dr. Seger noted the possibility of particle orientation in clays and fine-grain ceramic pastes during molding. It was determined in [5–7] that particle orientation in clays and ceramic pastes brings about changes in shrinkage in different directions and can cause deformation and cracking of articles. In blanks obtained by extrusion the particles are oriented so that their main transverse surfaces are arranged along the direction of motion of the paste and form an axisymmetric structure [1, 5, 6]. It was also noted that the main surfaces of quartz and feldspar grains lie on planes coinciding with the (001) planes of the clayey particles surrounding their aggregates, and these planes are found to be parallel to the surface of the article obtained by casting or plastic molding [4, 5]. These phenomena are clearly seen in non-fired and fired articles. In addition, glazed porcelain is a composite material, whose surface is covered by a layer of glaze glass with an intermediate layer that bonds the glass to the ceramic matrix. The thickness and character of the inter-

¹ Gzhel' State Artistic and Industrial Institute, Gzhel', Moscow Oblast', Russia; Keramika Gzheli, JSC, Gzhel', Moscow Oblast', Russia (e-mail: nektan25@yandex.ru).

² D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia (e-mail: alezakharov@rambler.ru).

TABLE 1. Chemical Compositions of the Experimental Pastes

Composition	Content, wt. %								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	other, %
1	65.24	23.26	0.35	0.50	0.73	0.36	2.48	0.84	6.24
2	60.26	28.55	0.34	0.45	0.30	0.20	2.20	0.4	7.30

TABLE 2. Main Molding Parameters of the Experimental Articles

Molding method	Molded article	Wall thickness, mm	Mold material	Moisture content of paste, %
Drain slip casting	Hollow, tureen	3 – 4	Gypsum	30
Drain slip casting with vacuum suction	Hollow, cup	2.5	Gypsum	29
Filling slip casting	Flat, cutting board	7 – 9	Gypsum	30
Filling slip casting under pressure *	Flat, platter with detailed edge	4.5 – 5	Synthetic plastic	–
Rolling **	Flat, saucer	2.7 – 3	Gypsum	19 – 22
Rolling	Flat, goblet	3.5	Gypsum	19 – 22
Isostatic pressing ***	Complexly shaped article with variable thickness	To 100	Polyurethane	To 3

* Pressure 2.5 MPa, suspension density 1.78 g/cm³.

** Force developed in the molding process 304 N at the corresponding rotational frequencies of the roller (200 min⁻¹) and spindle (500 min⁻¹) [9].

*** Pressing pressure 90 MPa.

mediate layer depend on the compositions of the paste and glaze, the structure of the base, the particulars of the glazing and the conditions of glaze firing. The glaze layer has a large effect not only on the properties of articles (strength, thermal stability and so forth), but it also greatly increases the danger of the article becoming deformed during firing [8].

The aim of the present investigation was to determine the relation between the molding method and the structural particulars of the glazed porcelain material.

Hollow and flat porcelain articles (cups, saucers, salad bowls, tureens, cheeseboard) with wall thickness 2 – 9 mm as well as an electrical insulator with thickness to 100 mm were chosen as samples. The articles were fabricated from pastes designed to obtain hard (composition 1) and electro-technical (composition 2) porcelain, whose compositions are presented in Table 1.

The samples were obtained by the following methods: isostatic pressing (electrical insulator), rolling (saucers, goblets and cups), drain and filling slip casting in gypsum molds (cups, tureens, sugar bowls, candy dishes, cutting boards, spoons), drain slip casting into gypsum molds using vacuum suction (cups, soup cups) and filling slip casting under pressure into plastic molds (salad bowls, saucers, tureens). The main molding parameters are presented in Table 2.

The investigation was performed on transverse sections of a wall of fired porcelain articles by means of optical microscopy. An elongated fragment shape of quartz grains was

characteristic for the structures of all samples in this work. This shape was obtained by the impact of milling bodies during wet milling in ball mills.

RESULTS AND DISCUSSION

Drain Slip Casting

The porcelain samples obtained by slip casting into gypsum molds are distinguished by pronounced orientation of the particles [2]. The surface of the article facing the gypsum mold is enriched with clayey particles with a low content of large (> 40 μm) grains of stony materials. The main layer of the material, where stony and clayey particles are present, is formed at distances 150 – 250 μm from the surface.

A unique separation effect occurs on the inner wall of the article after the excess slip drains and subsequent moisture filtration into the bulk of the cast is completed: the clayey particles migrate into the casting, partially uncovering the grains of the stony materials. The zone is no more than 200 μm wide. A marked orientation of elongated, fragment-shaped particles (quartz, feldspar) parallel to the surface of the article is observed in the sample.

After the glaze firing more intense growth of small mullite needles in the contact layer of the porcelain and glaze on the article surface facing the gypsum mold during the casting process is observed [2]. The formation of regions

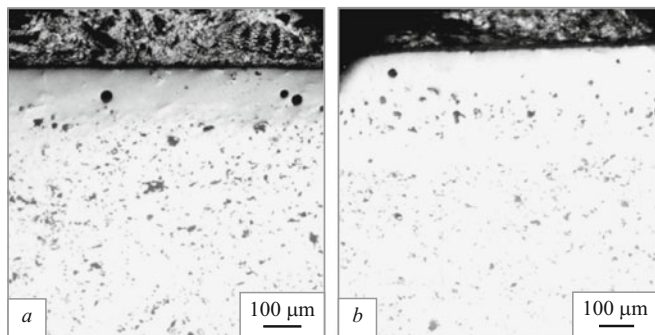


Fig. 1. Microstructure of a fired sample (in reflected light) fabricated by drain casting.

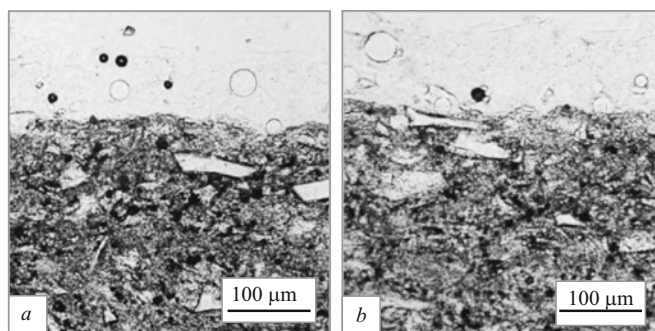


Fig. 2. Microstructure of the fired sample, fabricated by means of drain casting with vacuum suction, in transmitted light: *a*) surface of the article, turned toward the mold; *b*) surface turned toward the suction system.

with pronounced orientation and different concentration of clayey and stony particles affects the formation of porosity in the article. Differences in the porosity on different surfaces of the article are clearly seen in a photograph of the structure of the samples in reflected light (Fig. 1). It should be noted that the glaze coating on the samples presented, which can be easily identified according to rare, more rounded and large pores, is 100 – 115 μm thick.

Drain Slip Casting with Vacuum Suction

The article's outer surface facing the gypsum mold (Fig. 2*a*) is structurally reminiscent of a sample obtained by ordinary slip casting. The orientation of the particles parallel to the article's surface is observed in a layer up to 250 – 300 μm thick. Subsequently, the particles are arranged mostly chaotically, and only nearby at distances about 50 – 70 μm from the inner surface of the article they are packed so that their main planes are parallel to it (Fig. 2*b*). The separation of the casting on the slip drain side, an effect characteristic for ordinary drain casting, is very weakly expressed here. This phenomenon can be explained by a change in the method by which the excess slip is removed. In this molding method, after the wall has been accumulated on the surface

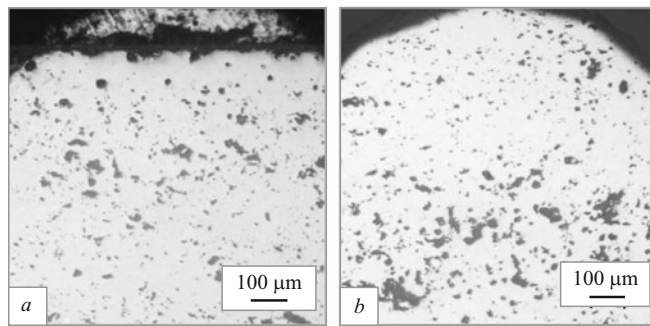


Fig. 3. Microstructure of fired sample, fabricated by filling casting, in reflected light: *a*) article's surface facing the mold; *b*) center of the wall of the article with a characteristic seam.

of the gypsum mold in 4.5 min the excess slip is removed into two devices through a suction system with the aid of a vacuum. The particles of the material in the still soft viscous casting on the drain side strive to follow the flow of the removed material and as a result lose an oriented position. The surface of the article on the slip removal side is less smooth than on the mold side, but this does not result in any significant differences in the formation of the glaze layer.

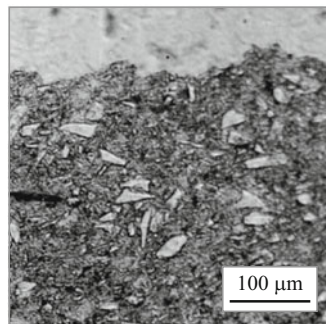
Filling Slip Casting

The porcelain samples obtained by this method differ by the presence of a characteristic, visually noticeable, central zone in the form of a strip up to 200 μm thick, enriched with quartz grains [2]. The structures of the surfaces of the article (Fig. 3*a*) facing two sides of a gypsum mold are similar to the structure of the exterior side of the casting made by the usual casting method. The formation of a central zone (seam) with larger and irregularly shaped aggregates of pores (Fig. 3*b*) in comparison with the porosity near the surfaces (Fig. 3*a*) is clearly visible in the photographs of the sample's structure in reflected light.

Filling Slip Casting under Pressure in Polymer Molds

In this molding method the casting is formed between two sides of a polymer mold, through the pores and special outlet openings of which the moisture is removed under pressure. A central seam, reminiscent of the central zone of a casting obtained by the usual filling method but not so pronounced, can be seen visually on the wall of the article being formed. A unique structure, noticeable on dry and fired samples, forms on both sides of the central opening of width about 1600 μm (Fig. 4). 'Streams' of width 50 – 100 μm , enriched alternately with either clayey or stony particles, rush vertically or at an angle toward the surface of the mold from a depth of about 1400 – 1700 μm . As one can see in the photographs, the particles of the stony materials in the 'flow' can be oriented parallel to the article's surface or along the 'flow'. This phenomenon can be explained by the construction of the mold and the applied pressure, which make it pos-

Fig. 4. Microstructure of fired sample, fabricated by casing under pressure, in transmitted light.



sible to remove the filtrate rapidly. At the location of the outlet openings the distance between the surface of the mold and the outlet channel is about 6 – 8 mm, and moisture is filtered out of the slip at these points more intensely, which is what gives rise to the flows in the casting.

Plastic Molding (Rolling)

In plastic molding by rolling the article is formed between a gypsum mold and a roller or template. The exterior side of the hollow article (goblet) is formed on the surface of a gypsum mold (Fig. 5a) and the interior side is rolled with a roller (Fig. 5b). For a flat article (saucer) the interior side lies on the surface of the gypsum mold (Fig. 6a), and the exterior side with a foot is formed by rolling with a template (Fig. 6b). On rolling in both cases large particles (quartz grains larger than 40 – 50 μm) occupy a position in which their main planes are parallel to the surface. Mainly, the regions with oriented quartz grains are located near the surface formed by the roller. The arrangement of the particles is most disordered in the zones of the foot and change in the contour of the article. Sometimes, sections of the structure with a chaotic arrangement of the particles are encountered near the surface which in the process of molding was turned toward the gypsum mold; hypothetically, these could be a puddle arising with sloppy packing of the paste into the mold or as a result of inheriting the texture of a blank obtained by extrusion. Examination of fired samples showed that the glaze layer is 5 – 8% thinner on the surfaces of articles formed by rolling than on the side which was turned toward the gypsum mold. This phenomenon is probably due to the compaction of the material on the surface of the blank formed by a template.

Isostatic Pressing

The sample of technical porcelain was fabricated using granular powder obtained in a spray drier. Granules ranging in size from 130 to 300 – 350 μm, closely packed but not fractured, can be seen on the fresh cleavage face of a dry sample. Examination of thin sections of fired articles in polarized light under a microscope reveals traces of boundaries of the initial granules in the form of rings formed by quartz grains (Fig. 7). The latter phenomenon could be caused by

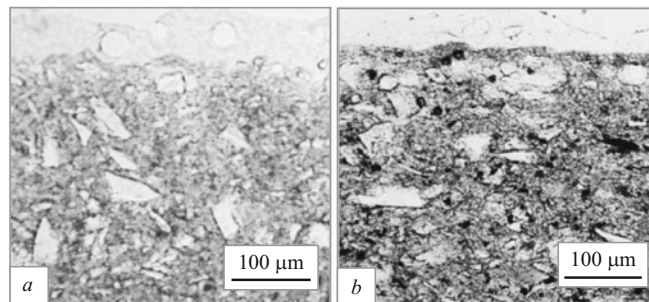


Fig. 5. Microstructure of a hollow fired sample (cup), fabricated by plastic molding, in transmitted light: a) article surface turned toward the mold; b) surface rolled by roller.

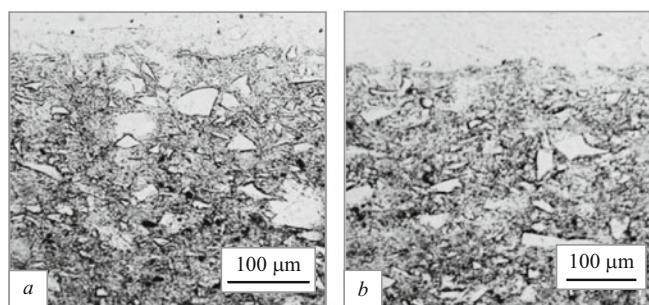


Fig. 6. Microstructure of a flat fired sample (saucer), fabricated by plastic molding, in transmitted light: a) article surface facing the mold; b) surface rolled by roller.

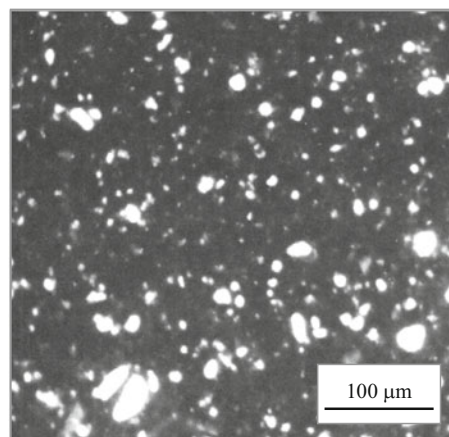


Fig. 7. Microstructure of fired sample of electroporcelain fabricated by isostatic pressing, in polarized light.

the texture formed by the granules themselves at the time they are fabricated [10].

The present investigations have established that molding methods affect the creation of the structure of a porcelain article. Regions with pronounced orientation and different concentration of clayey and stony particles were found. It was found the characteristic features of the molded structure of an article are related with the likelihood of defects appearing.

Thus, a structure with the highest degree of particle orientation and the highest surface uniformity is formed during drain casting; specifically, deformation defects as well as cracks and casting spots most often form in precisely these articles during the fabrication process.

It was also established that the molding method influences the thickness and the character of the contact between the glaze layer and the porcelain. Small differences in the values of these parameters of the glaze were observed on different surfaces of the same article.

It was confirmed that the structure of a porcelain article inherits the character of the texture for molding specially prepared pastes (in plastic molding and isostatic pressing). In the latter case the interior structure of the granules of the press powder is retained in the article, even though a significant pressing force is applied.

REFERENCES

1. A. P. Pyzhova, V. V. Korobkina, and V. S. Kosov, *Defects in Fine-Grain Ceramic Articles: Causes and Methods of Elimination* [in Russian], Legprombytizdat, Moscow (1993).
2. T. L. Neklyudova and G. N. Maslennikova, "Structural particulars of porcelain articles manufactured by slip casting," *Steklo Keram.*, No. 2, 16–19 (2011); T. L. Neklyudova and G. N. Maslennikova, "Structural particulars of porcelain articles manufactured by slip casting," *Glass Ceram.*, **68**(1–2), 52–55 (2011).
3. A. I. Zakharov, "Homogeneity of ceramics: association with the molding method and geometrical parameters of articles," *Steklo Keram.*, No. 9, 35–38 (2003); A. I. Zakharov, "Homogeneity of Ceramics: Correlation with Molding Method and Geometrical Parameters of Articles," *Glass Ceram.*, **60**(9–10), 287–290 (2003).
4. A. I. Zakharov and I. A. Karnaushchenko, "Capillary suction study of the surface homogeneity of intermediate ceramic parts and articles," *Steklo Keram.*, No. 10, 37–40 (2008); A. I. Zakharov and I. A. Karnaushchenko, "Capillary suction study of the surface homogeneity of semifinished ceramic products and articles," *Glass Ceram.*, **65**(9–10), 358–361 (2008).
5. W. O. Williamson, "Particle orientation in clays and fine-ceramic articles and its relation with forming processes," in: *Ceramic Fabrication Processes* [Russian translation], Izd. Inostr. Lit., Moscow (1960).
6. V. I. Osipov, *Nature of the Strength and Deformation Properties of Clayey Rocks* [in Russian], Izd. MGU, Moscow (1979).
7. I. Ya. Yurchak, "Effect of the orientation of the paste particles on the deformation of porcelain articles," *Tr. GIKI*, No. 1, 24–36 (1956).
8. A. I. Zakharov, I. A. Karnaushchenko and D. V. Andreev, "Effect of article shape on the particulars of the technology and formation of defects," in: E. S. Lukin, A. V. Belyakov, N. A. Makarov, et al. (compiled), *D. N. Polyboyarinov (1899–1975): at the Sources of Domestic Industry* [in Russian], RKhTU, Moscow (2009), pp. 304–316 (famous graduates of the D. I. Mendeleev Russian Chemical Technology University, Moscow, Russia).
9. B. S. Kondrat'eva, V. G. Lyaburkin, V. G. Panteleev, et al., "Study of the relation between the properties of molds, pastes and equipment parameters in the molding process: Study of ceramic raw materials and improvement of technological processes in the production of porcelain articles," in: *Collection of the Scientific Works of VNIIF* [in Russian], TsNIITEIlegprom, Moscow (1991), pp. 55–62.
10. *The Process of Production of Ceramic Tiles: Technologies Used and New Advances*, Association of Italian Manufacturers of Machinery and Equipment for the Ceramic Industry, ACIMAC, Moscow (2004).